STUDIES ON THE RAPID TANNAGE OF HEAVY LEATHERS

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The studies on the rapid tannage of heavy leathers revealed that the rate of penetration increased when the pelt was brought to isoelectric point before vegetable tanning. Osmotan process and chrome pretreatment method gave leathers of good yield and desirable physical properties. Tanning at higher temperatures facilitated the most rapid penetration as expected, but the feel and physical properties of leather were not very satisfactory. This process needs modification; the temperature should be carefully controlled to avoid damages to the fibres during tanning.

Introduction

The problem of rapid tanning has been engaging the attention of the tanners all over the world for the last forty years. This has gathered momentum especially after the introduction of the synthetics and now the very survival of sole leather depends on the rapid tanning procedures without detriment to its inherent properties.

Sole leather should be strong and reasonably tough, besides possessing good abrasion resistance and low water absorption. A good colour is desirable since it appeals to the selective taste of the buyers. Sole leather should possess a high degree of tannage and low water soluble content; the yield is equally an important factor. Hence these aspects deserve careful consideration in the study of rapid tannage of sole leather.

Pawlowitsch[1] studied the rate of penetration at different pH levels and temperatures of the tannin infusions. Later Belavsky and Fiksl[2] stressed on the proper co-ordination of concentration, temperature and pH of tan liquors. The increase in the strength of liquors brings about peptisation and aggregation of the tannin particles, the former more so at relatively high concentrations. Rise in temperature as well as decrease in acidity increase the degree of dispersion of the tannin molecules facilitating penetration. Increase in pH also lessens the affinity of the tannin for the pelt. Therefore, rapid colouring of the pelt is facilitated at higher pH while an increase in acidity assists the combination of tannin and pelt.

In 1943, Humphreys[3] suggested a 3-pit strong liquor tannage and since then many methods of rapid tannage have been evolved. But in most of these tannages, the tail liquor is not easily exhausted, though some methods are claimed to have overcome this difficulty.

Atkinson and Cutting[4] devised a simple and rapid pit-cum-drum tannage where waste liquor left in the drum at the end of the 36 hours was withdrawn and diluted to 15°Bk in a pit for use in the pretannage of fully delimed hides.

Further investigations of Humphreys and Chand[5] revealed that the yield of leathers increased from 61 to 69%, with the increase in tannins from 28 to 30%. A simple two-pit system of rapid tannage was also developed by them.

Herfeld[6] observed that (i) the sapping of tan liquors is accomplished by the counter current principle which helps in the uptake of the coarsely dispersed particles through a selective absorption of tannins, (ii) the concentration of liquor should be increased within a relatively short time, (iii) pH should be properly adjusted during tanning, (iv) rise in temperature imparts better solubility and reduction in particle size, increasing the rate of tannage and reducing the risk of sludge formation, (v) pelt should be completely delimed and pretanned suitably.

On the tannins velocity, Woolenberg[7] found that the duration of tanning was reduced by a factor 2·6 by raising the temperature from 8 to 18°C and by a factor 2 by increasing the strength of the liquor from 80 to 140°Bk. He also suggested the use of a suitable tanning mixture of low viscosity as well as a drum in the intermediate stage maintaining the liquors at as high a temperature as permissible.

Two processes have been recently developed in South Africa viz., Osmotan process and Liritan no-effluent process[8]. The former avoids the usual deliming; the unhaired hides are pickled in 1·5% H_2SO_4 and 10% NaCl for a day and then kept in tan liquor (25°Bk) at pH 3·0. Deliming is completed during surface tanning. Then the hides pass through four tan pits with the tan liquor varying from 60 to 80°Bk while the pH rises from 3·1 to 3·3. The hides remain for one day in each pit and the counter current system is followed.

In the Liritan process, the hides are delimed for 72 hours and pickled with 1·25% H_2SO_4, 5% NaCl and 2% calgon. Surface tanning is done in a pit with 20°Bk liquor at pH 3·0. The hides are then entered into strong liquors (67-100°Bk). They are finally drummed with powdered wattle extract and fillers.

Various methods of pretreatments before the vegetable tannage are suggested in the literature. The pretanning agents employed are: chrome, chrome or aluminium complexes with syntans, dialdehyde starch,[9] alkali metal nitrites, syntans, formaldehyde, calgon and polysaccharide bisulphites.

Attempts have also been made to precondition the pelt to the required pH by treatment with buffers prior to vegetable tanning. It has been conclusively shown[10] that the pelt brought to the isoelectric point can be tanned straight in pits with warm strong tanning liquors. The tanning takes place without shrinkage or hydrolysis; for a heavy hide, it takes about one week for getting struck through and two weeks to give the maximum yield.

In our experiments, some less expensive pretanning operations were follow-

ed with slight modifications to suit our conditions, and their effect on the speed of penetration, extent of fixation and the quality of leather studied.

The following pretanning/preconditioning systems were tried:

I. Preconditioning the pelt to pH 4·8 Buffers used:

a. (i) Sodium acetate (0·1M) + citric acid (0·1M)
   (ii) Sodium citrate (0·1M) + citric acid (0·1M)
b. 1% boric acid solution with dil. HCl
c. 1% HCHO solution with HCOOH

II. Pickling:

a. 5% NaCl + HCl in just sufficient quantity to maintain the pH at 4·5-4·8.
b. Osmotan processes: H_2SO_4 + NaCl

III. HCHO pretreatment

IV. Chrome pretreatment

V. Tanning at higher temperature

VI. Limed pelt treated straight with bisulphited wattle liquor.[12]

VII. Control (delimed with boric acid and wattle tanned).

Experimental

Wet-salted buffalo hide was soaked and limed as followed in sole leather manufacture. After unhairing, fleshing and washing, pieces (20×20 cm.) were cut from the butt portion. The pieces were weighed (each piece approx. 200 g.) and then taken for tanning.

I(a). For buffer pretreatment, the pieces were completely delimed with boric acid, washed well and then placed in respective buffer solutions for about 48 hours to attain equilibrium pH of 4·8. 0·1 Molar solutions were used and a uniform float (400% on pelt weight) was employed. A few drops of thymol dissolved in acetone were added to prevent putrefaction of the pelt. The pH was maintained at 4·8 by occasionally adding citric acid or acetic acid.

I(b). The pelt was delimed with boric acid and then left in 1% boric acid solution (float 400%). Dilute hydrochloric acid was added occasionally to maintain the pH at 4·8 and the pelt was left for about 48 hours.

I(c). In the case of HCHO treatment, 1% HCHO[11] was used with a 400% float and the pH adjusted to 4·8 with formic acid.

II(a). Limed pelt was pickled with 5% NaCl and dilute hydrochloric acid was added in small amounts. The pelt was frequently handled till pH was approximately 4·8. (b) Limed pelt was pickled with NaCl and H_2SO_4[13] as in Osmotan process.

III. Delimed pelt was pretreated with 1% HCHO in 400% float for 48 hours.

IV. For chrome pretreatment,[4] the pelt was delimed and pickled with 1·25% H_2SO_4 and 6% NaCl. It was then chrome-tanned using a liquor with 0·6% Cr_2O_3 content (on pelt weight) and 48% basicity. Penetration was found completed in 36 hours; vegetable tanning was then commenced.

V. For tanning at higher temperature, pelt was completely delimed with boric acid, washed and then kept in 50°Bk wat-

tle liquor (35-40°C). After 24 hours, the temperature was raised to 40-50°C. The strength of liquor was raised to 70°Bk after 3 days and the temperature maintained at 45°C for the rest of the tanning period.

VI. Modified bisulphited[12] wattle liquor was prepared using 1 part wattle extract, 1 part water and 10-12% sodium bisulphite. Then HCOOH was added to bring down the pH to 3·0-3·2 and the liquor was diluted to 70°Bk. Limed pelt was kept straight in this liquor.

VII. For the control, pelt was delimed completely with boric acid and then vegetable tanned.

All these pretanning/preconditioning operations were carried out in glass troughs (25 cm. diameter) under laboratory conditions. The subsequent tannages were carried out in the same troughs after draining the liquors.

Vegetable tanning

In the Osmotan process, the pickled pelt was placed in 25°Bk wattle liquor at pH 3·0 for 24 hours before its transfer to 60°Bk liquor. The pelt was then successively tanned in 67°, 74° and 80°Bk liquors at intervals of one day using the counter current principle. 400% float (on pelt weight) was employed in all the cases. The tanning was completed in only five days.

For the control, the delimed pelt was first placed in 25°Bk liquor for 24 hours. The strength was raised to 50°Bk and after three days, to 70°Bk.

The chrome pretreated pelt was vegetable tanned with 50°Bk liquor in the first three days the strength of the liquor being then raised to 70°Bk.

The tannages for 'tanning at higher temperature' and 'tanning of limed pelt

Table 1

RATE OF PENETRATION, COLOUR, FEEL AND YIELD OF LEATHERS

Treatment	Penetration time (days)	Colour	Feel	Yield (%)
I. a. (i) $NaAc + HAc$	6	Same as control		64
(ii) $NaCi + HCi$	6		„	34
b. Boric acid	7		„	63
c. HCHO	7	Same as control	Slightly tougher	61
II. a. NaCl + HCl	6	Better than control	Same as control	59
b. Osmotan process	4	Darker than control	Tougher	67
III. HCHO pretreatment	7	Same as control		56
IV. Chrome pretreatment	7	Darker than control	Tougher	65
V. Tanning at higher temperature	3½	„	Softer and a little spongy	55
VI. Limed pelt	6	Very good	Softer	56
VII. Control	9	Good	„	56

with bisulphited liquor' were done as described earlier.

The buffer treated pieces were kept straight in 50°Bk wattle liquor and tanned for 3 days; the strength of liquor was raised to 70°Bk and the tannage completed.

The pH of wattle liquor was adjusted to appropriate levels in Osmotan process and in the experiment with bisulphited wattle liquor. In all other cases, wattle liquor at its natural pH was used throughout.

In experiments except Osmotan process, the duration of tanning was 12 days and the total amount of tannins given was about 30% (on pelt weight). In Osmotan process, the amount of tannins could not be calculated since the counter current method was adopted.

After the completion of the tanning, the pieces were washed, lightly scrubbed on the surface, very lightly oiled and allowed to dry. No bleaching or myrobing was given.

During tannage, the time taken for complete penetration in each case was noted. The tanned pieces were also assessed for their feel, colour and yield (Table 1). The leathers were analysed for important physico-chemical properties like degree of tannage, abrasion resistance and water absorption. The resutls are presented in Tables 2 and 3.

Discussion

From Table 1, it may be observed that the time required for complete penetration is shortened in all the pretanning/preconditioning systems compared to the control. Adjustment of pH of the pelt to 4·8 (i.e.p.) either by use of buffer salts or by boric acid and hydrochloric acid, prior to tanning, facilitated

Table 2

CHEMICAL ANALYSIS OF LEATHERS

	Moisture (%)	Oils and fats (%)	Water solubles (%)	Total ash (%)	Insoluble ash (%)	Hide substances (%)	Degree of tannage
I. a. (i)	15·5	0·50	7·8	0·45	0·20	42·94	76·7
(ii)	14·5	0·40	10·4	0·50	0·24	42·34	75·8
b.	14·2	0·61	10·4	0·60	0·25	45·68	70·46
c.	14·5	0·50	4·0	0·55	0·23	43·00	87·00
II. a.	13·5	0·46	5·9	0·60	0·26	45·00	77·40
b.	14·1	0·60	7·5	0·62	0·30	41·50	86·70
III.	13·3	0·41	4·2	0·56	0·30	49·90	63·5
IV.	15·0	0·58	4·9	*1·50	1·24	48·50	59·8
V.	14·6	0·60	9·3	0·42	0·30	47·00	60·0
VI.	13·4	0·52	10·48	0·58	0·24	45·55	65·4
VII.	13·7	0·50	4·5	0·48	0·25	51·75	56·3

*Cr_2O_3 content 1·1%

quicker penetration which was completed in 6-7 days as against 9 days (control).

Rise in temperature of tan liquor leads to rapid penetration and the pelt is struck through in 90 hours. But prolonged treatment in hot liquor impairs the structure of the pelt. The tanned piece was a little spongy and its chemical and physical characteristics were not comparable to those of the control.

Osmotan process yielded rapid penetration; in the case of limed pelt tanned straight in modified wattle liquor, penetration was completed in less than six days. Osmotan process gave the highest yield (67%) followed by chrome retan process (65%). In the tannages with buffer treatments, the yield varied between 61% and 64%; tanning at higher temperature and straight tanning of limed pelt gave comparatively low yields. The buffer treated leathers gave almost the same feel and colour but better compactness than those of the control. Limed pelt tanned straight with modified wattle liquor gave leathers with very good colour but with less fullness and softer feel. Formaldehyde treated leather was fuller and tougher than that of the control. Osmotan, chrome pretreatment and tanning at higher temperatures gave darker leathers; in the former two, leathers were tougher.

Table 2 shows that HCHO pretreatment and the Osmotan process give high degree of tannage. The buffer treated samples have good tannin fixation, the degree of tannage ranging 70-76%. But these leathers possess comparatively higher water solubles content (7·8-10·4%). In the other experiments, the degree of tannage is about 60% as compared to 56·3% in the control.

Except in Osmotan and chrome pretreatment processes, there is less abrasion resistance and more water absorp-

Table 2

PHYSICAL TESTING OF LEATHERS

	Abrasion resistance Loss of thickness (mm)/		Water absorption (%)		T_s (°C)
	100 revns.	500 revns.	2 hr.	24 hr.	
I. a. (i)	1·79	4·44	60·8	67·3	87
(ii)	2·05	4·69	64·1	70·1	87
b.	2·38	5·00	65·2	70·1	86
c.	1·81	4·62	62·2	67·8	88
II. a.	1·96	4·52	66·1	72·9	86
b.	1·73	3·40	54·0	58·1	88
III.	2·24	5·00	61·3	65·2	85
IV.	1 93	4·05	56·1	58·5	89
V.	1 91	4·55	62·0	67·1	82
VI.	1·93	4·75	68·3	72·4	86
VII.	1·96	3·89	55·2	59·2	85

tion in all other cases as compared to the control (Table 3). In the case of Osmotan, the physical properties are slightly improved while in chrome pretreatment, the properties are almost the same as those of the control. In other pretanning/preconditioning systems, penetration is quicker and fixation greater; but some of the physical properties are not comparable to those of the control. As one of the most rapid tanning processes, Osmotan process alone imparts the required physical characteristics of normal sole leather, despite its disadvantages like lack of simplicity and need for adequate control.

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